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AUTOCLAVED LIME-QUARTZ MATERIALS I. SOME FACTORS INFLUENCING STRENGTH

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ABSTRACT

Autoclaved materials were made with varying bulk C/S ratios and quartz particle sizes, with and without added kaolinite, and their strengths, densities, phase and C-S-H compositions and porosities determined. If much unreacted quartz remains, strength is controlled by its particle-size distribution and the porosity, but if the material is largely C-S-H, the distribution of particle types within the C-S-H has a major effect. Increase in C-S-H crystallinity can either raise or lower strength depending on the amount of unreacted quartz. Addition of kaolinite raises the crystallinity of the C-S-H and may also accelerate its formation.

حضرت المواد المعالجة بخاريا باستخدام نسب مختلفة من اكسيد الكالسيوم الى السليكا مع اختلاف حجم حبيبات الكوارتز ايضا باضافة او عدم اضافة الكاولينيت وعينت قوة تحمل الضغط والكثافة النسبية والتركيب المعدني للمادة الرابطة ووجد انه في حالة تبقى كمية كبيرة من الكوارتز غير المتحد فان تحمل الضغط يتحكم فيه حجم حبيبات السليكا ومسامية الجسم، ولكن اذا كانت نسبة المواد الرابطة هي الغالبة فان انواع الاخير لها التأثير الاكبر وزيارة تبلور المادة الرابطة يمكن ان يرفع او يخفض قوة تحمل الضغط وهذا يعتمد على كمية الكوارتز غير المتحد اما اضافة الكاولينيت فانه يرفع درجة تبلور المادة الرابطة ويمكن ان يساعد على سرعة تكوينها .

Introduction

Autoclave processes in which lime and quartz are the starting materials are used to make calcium silicate bricks and various other products. Despite many previous studies, several aspects of the reaction are still incompletely understood. One is the effect on strength of crystallization of the binder. Early views that maximum formation of crystalline tobermorite is desirable are now generally rejected, except probably for aerated concrete and other low-density products. There is, however, no agreement as to whether crystallization of this phase is irrelevant, undesirable, or desirable to the extent that a blend of crystalline and amorphous particles is required. A second problem concerns the effect of over-reaction, whether caused by too long a time or too high a temperature of autoclaving or by the presence of too much fine quartz. Finally, the effects of adding kaolinite or other suitably reactive sources of Al^{3+} do not seem to be clearly understood. The present work was done to clarify these points.

Experimental

Sample Preparation, Compressive Strengths and Bulk Densities

The silica was a quartzite from Ballarat, Victoria, Australia; five particle-size fractions were used, ranging from below 7.5 μm to above 45 μm . The SiO_2 contents were 98.5 - 99.8%, the coarser fractions being the purer, with Al_2O_3 and Fe_2O_3 the chief impurities. The $Ca(OH)_2$ was reagent grade material. Two series of specimens were made, one using $Ca(OH)_2$ and quartz only, and the other with the addition of 1% of kaolinite on the dry weight. Specimens were made with bulk C/S molar ratios of 0.50, 0.81, 0.99 and 1.32. In each case, a paste was first made with water; to achieve reasonable workability, a different water: solids ratio had to be used for each C/S ratio (0.213, 0.226, 0.240 and 0.253 respectively). The paste was cast into a 100 x 13 x 13 mm bar, compacted by machine tamping, cured in the mould for 24 h at 100% R.H. and room temperature, demoulded, autoclaved for 12 h of which 8 h was at 177°C, and finally kept in water for 24 h at room temperature. Three separate mixes were usually made for each combination of bulk composition and quartz particle size, and two bars made from each mix.

The bars were cut into 13 mm cubes and compressive strengths of 3 cubes from each bar tested saturated. The bulk density of one cube from each mix was determined by weight and volume measurement after drying for 24 h at 127°C. From the totality of specimens, 42 representative ones were chosen for further study.

Insoluble Residue and CO_2 Determinations

The insoluble residue was used as a measure of unreacted quartz, and was usually determined thus. The sample (1 g) was slurried with a little water; 2M HCl (50 ml) was added and the suspension digested for 1 h at room temperature. It was then filtered through a 0.8 μm millipore filter and the residue washed 8 times with warm water. The filter paper and its contents were warmed with 10% $NaOH$ (10 ml) until the paper

dissolved. The mixture was diluted to 100 ml with hot water and let stand for 30 min. The solution was reacidified to methyl red, filtered, and the residue washed as before. The residue was ignited for 1 h at 950°C before weighing.

For samples made with the finer quartz fractions, this method gave slow filtration and the following was substituted. The sample (1 g) was mixed with NH_4Cl (1 g) and conc. HCl (10 ml) carefully added. When the reaction subsided, conc. HNO_3 (2 drops) was added. The mixture was heated on a water bath for 30 min with occasional stirring. Filtration, washing, NaOH treatment and weighing were done as before.

Carbon dioxide was determined by heating at 900°C in N_2 and absorbing the evolved gas in $\text{Ba}(\text{OH})_2$ solution followed by back-titration with HCl . The CO_2 was assumed to occur wholly as CaCO_3 .

X-Ray Diffraction

X-ray diffractometer traces were made of all samples at a scanning rate of 2 deg/min; selected samples were also examined at a slower scanning rate or with a Guinier camera. All samples were found to contain unreacted quartz; some contained unreacted $\text{Ca}(\text{OH})_2$. Poorly crystalline C-S-H was detected in most samples by a broad band at 3.1 - 2.7 Å, peaking at about 3.04 Å, together usually with a weaker and sharper peak at about 1.82 Å. In a few samples, the 3 Å band had shoulders or very weak subsidiary peaks at 3.08 Å and sometimes also 2.98 and 2.82 Å, attributable to incipient crystallization of tobermorite. No other peaks of C-S-H or tobermorite were observed. Calcite was detectable as a minor constituent of most samples by its strongest peak, which was superimposed on the C-S-H band. In a few samples made with the coarser quartz fractions, two or three of the strongest peaks of $\alpha\text{-C}_2\text{SH}$ were weakly observable.

Differential Thermal Analysis and Thermogravimetry

All samples were studied by DTA at 10 deg min^{-1} to test for quartz, $\text{Ca}(\text{OH})_2$, CaCO_3 , C-S-H and $\alpha\text{-C}_2\text{SH}$. Where $\text{Ca}(\text{OH})_2$ was present, part of the cooling curve was studied to test for the quartz transition. The C-S-H gave a broad endotherm below 300°C and an exotherm at 800 - 890°C. The C/S ratio of the C-S-H was calculated as described later, and with decrease in its value the exotherm moved to lower temperatures and became sharper, as observed previously (1,2). Variation in peak temperature was continuous; a few samples gave double peaks. These results suggest that the C/S ratio of the C-S-H varies continuously and that some samples contained C-S-H of more than one composition. Some specimens containing C-S-H of high C/S ratio also gave a weak endotherm at 680 - 740°C; similar peaks have been reported earlier (2). Its significance in the present case is uncertain. It could be a feature of the C-S-H decomposition, but might also be due to CaCO_3 , which can give multiple peaks under certain conditions (3).

TG curves were made for all samples at 10 deg min^{-1} in N_2 . They showed a continuous loss up to about 700°C on which were superimposed relatively sharp steps attributable to $\text{Ca}(\text{OH})_2$ and CaCO_3 at about 450°C and above 700°C respectively.

$\text{Ca}(\text{OH})_2$ was determined from the TG curve and also by DTA. In the latter method, standardized conditions were used and calibration effected by using mixtures containing known amounts of $\text{Ca}(\text{OH})_2$ with various diluents. For samples with 10 - 30% $\text{Ca}(\text{OH})_2$ the two methods usually agreed to 1%; at higher $\text{Ca}(\text{OH})_2$ contents, the DTA results were usually higher than those from TG, while at low $\text{Ca}(\text{OH})_2$ contents, TG gave higher results than DTA and X-ray diffractometry was more sensitive than either. For most samples, the mean of the TG and DTA results was used but for $\text{Ca}(\text{OH})_2$ contents below 10% the TG values were used, except in a few cases below 3% where estimates based on the X-ray results were considered more reliable.

Results

Fig. 1 gives compressive strengths; each value is the mean for all the cubes of a given bulk composition and quartz particle size tested. Usually 18 cubes were tested, that had been cut from 6 different bars. Standard deviations are also given and relate to the means for the groups of 3 cubes cut from each bar. The broad trends are not altered if strengths are replaced by ratios of strength to bulk density.

For the 42 representative samples, weight percentages of C-S-H were calculated by difference, and volume percentages of each phase assuming densities of 2.71, 2.65, 2.24 and 2.20 g cm^{-3} for CaCO_3 , quartz, $\text{Ca}(\text{OH})_2$ and C-S-H respectively. Porosities were then calculated by difference. Table 1 gives the results, which refer to material dried at $110 - 127^\circ\text{C}$. It was assumed in the calculations that the calcium hydrosilicate

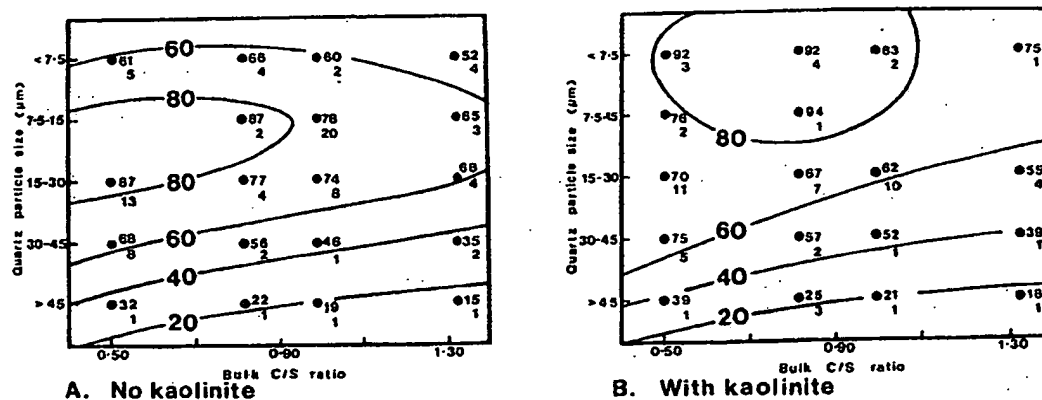


FIG. 1

Compressive strengths (MPa); means for all cubes of a given bulk composition and quartz particle size, with standard deviations below each value.

AUTOCLAVING, LIME-QUARTZ, KAOLINITE, CSH

TABLE 1
Strengths, Densities, and Compositional Data

No.	Quartz size	Bulk C/S	Bulk D	Comp. str.	Percent by weight				Composition of C-S-H		Percent by volume				
					(C-S-H sometimes includes α-C ₂ SH)						α-C ₂ SH				
	μm	molar	g cm ⁻³	MPa	CH	CC	Q	C-S-H	C/S	H/S	CH	CC	Q	C-S-H	Pores
No kaolinite															
1	> 45	0.50	1.65	32	19	3	57	21	2.39	1.17	14	2	35	16	33
2	"	0.81	1.58	22	30	3	47	20	4.00	1.94	21	2	28	14	35
3	"	0.99	1.54	19	38	3	41	18	3.64	5.12	26	2	24	12	36
4	"	1.32	1.51	15	46	3	35	16	3.53	2.17	31	2	20	11	36
5	30-45	0.50	1.59	74	1	5	46	48	1.60	0.92	1	3	27	35	34
6	"	0.81	1.51	57	16	3	38	43	2.04	1.31	11	2	22	29	36
7	"	0.99	1.52	46	24	6	36	34	2.22	0.78	16	3	21	24	36
8	"	1.32	1.44	34	31	4	30	35	2.81	2.11	20	2	16	23	39
9	15-30	0.50	1.44	101	0	1	32	67	0.99	0.80	0	1	17	44	38
10	"	0.50	1.46	73	0	1	32	67	0.99	0.80	0	1	18	44	37
11	"	0.81	1.39	77	0	1	20	79	1.32	1.15	0	1	10	50	39
12	"	0.99	1.35	78	1	3	18	78	1.54	1.26	1	1	9	48	41
13	"	1.32	1.35	68	6	7	16	71	1.87	1.40	4	3	8	44	41
14	7.5-15	0.99	1.22	100	0	2	5	93	1.09	1.20	0	1	2	52	45
15	"	0.81	1.23	87	0	1	17	88	1.02	0.90	0	1	5	49	45
16	"	0.99	1.23	67	0	5	10	85	1.19	0.93	0	2	5	47	46
17	"	1.32	1.23	68	2	2	10	86	1.70	1.83	1	1	5	48	45
18	< 7.5	0.50	1.22	60	0	5	28	67	0.83	0.77	0	2	13	37	48
19	"	0.81	1.21	63	0	2	10	88	0.99	0.99	0	1	5	48	46
20	"	0.99	1.17	59	0	2	9	89	1.22	1.28	0	1	4	47	48
21	"	1.32	1.19	54	1	2	10	87	1.74	1.91	1	1	4	47	47
With kaolinite															
22	> 45	0.50	1.65	39	13	3	54	30	2.36	2.13	10	2	34	22	32
23	"	0.81	1.57	26	27	2	45	26	3.28	2.40	19	1	27	18	35
24	"	0.99	1.55	22	36	2	40	22	2.68	1.77	25	1	23	16	35
25	"	1.32	1.51	18	45	3	34	18	2.84	1.32	30	2	20	12	36
26	30-45	0.50	1.61	78	3	3	47	47	1.79	1.63	2	2	29	34	33
27	"	0.81	1.53	57	11	5	38	46	2.42	2.09	7	3	22	32	36
28	"	0.99	1.50	51	17	2	33	48	2.52	2.60	11	1	19	33	36
29	"	1.32	1.45	39	28	2	28	42	2.65	2.43	18	1	15	28	38
30	15-30	0.50	1.46	87	0	7	34	59	0.97	0.92	0	4	19	39	38
31	"	0.50	1.42	71	0	1	34	65	1.11	1.33	0	1	18	42	39
32	"	0.81	1.39	78	0	2	23	75	1.48	1.52	0	1	12	47	40
33	"	0.81	1.40	60	0	1	20	79	1.35	1.62	0	0	11	50	39
34	"	0.99	1.37	58	0	1	17	82	1.57	1.63	0	0	9	51	40
35	"	0.99	1.38	89	0	1	18	81	1.61	1.48	0	1	9	51	39
36	"	1.32	1.36	57	6	2	15	77	1.91	1.65	4	1	8	47	40
37	7.5-15	0.50	1.30	76	0	2	28	70	0.90	1.18	0	1	14	41	44
38	"	0.81	1.25	94	0	2	10	88	0.99	1.18	0	1	5	50	44
39	< 7.5	0.50	1.23	91	0	2	29	69	0.96	1.57	0	1	13	39	47
40	"	0.81	1.21	95	0	2	12	86	1.05	1.23	0	1	6	47	46
41	"	0.99	1.21	83	0	6	11	83	1.22	1.24	0	3	5	46	46
42	"	1.32	1.21	74	3	3	11	83	1.71	1.75	2	1	5	46	46

was entirely C-S-H. In fact, α -C₂SH was detected by DTA in most of the samples made with the two coarsest quartz fractions and in three also by X-ray diffraction, but the X-ray and TG evidence indicated that the amounts present were small. The samples in which the C-S-H appeared from the X-ray evidence to have the highest crystallinity were mostly ones made using kaolinite and fine quartz.

The C/S ratios are 0.8 - 1.0 for samples made with the finest quartz and lowest bulk C/S ratio, and increase steadily with increase in either quartz particle size or bulk C/S ratio. They show little difference between the samples made with and without kaolinite. The values above about 3 are unreliable because they are much affected by errors in the determinations of unreacted quartz and Ca(OH)₂.

In Fig. 2, the compressive strengths of the representative samples are plotted against the volume percentage of C-S-H, the square of the gel: space ratio, and the C/S ratio of the C-S-H. The gel: space ratio is defined as the volume of C-S-H divided by the volume of C-S-H plus pores. The samples made using the two coarser quartz fractions nearly all have strengths below 55 - 60 MPa, while those made using the finer fractions nearly all have strengths above this range; the two groups can thus be distinguished on these plots. In Fig. 3 the compressive strengths of the representative samples are plotted against log porosities. There is no meaningful relationship for the samples as a whole and indeed, the strongest are among the most porous. However, if the samples are considered in groups made with quartz of a particular particle size, the results approximate to linear relationships between strength and log porosity, especially for the two coarsest quartz fractions. In none of these plots (Figs. 2 and 3) is there clear evidence of any difference between the samples made with and without kaolinite.

Discussion

The results confirm the findings of several earlier investigators that high strengths can be obtained in autoclaved materials in which the only reaction product is poorly crystalline C-S-H. The low crystallinity can be attributed to lack of space associated with relatively high bulk density (4).

There are marked differences between the samples made with the two coarsest grades of quartz and those made with the three finest, and the two groups will be considered separately.

Samples Made with Coarse Quartz

For the samples made with the two coarsest grades of quartz (above 45 and 30 - 45 μ m), the compressive strengths rise steadily with decrease in quartz particle size or bulk C/S ratio; addition of kaolinite marginally increases the strength (Fig. 1). For both quartz particle sizes, there is a high, negative correlation of strength with log porosity (Fig. 3). There are moderate correlations of strength with volume percentage of C-S-H, square of gel: space ratio, and Ca/Si ratio of C-S-H (Fig. 2).

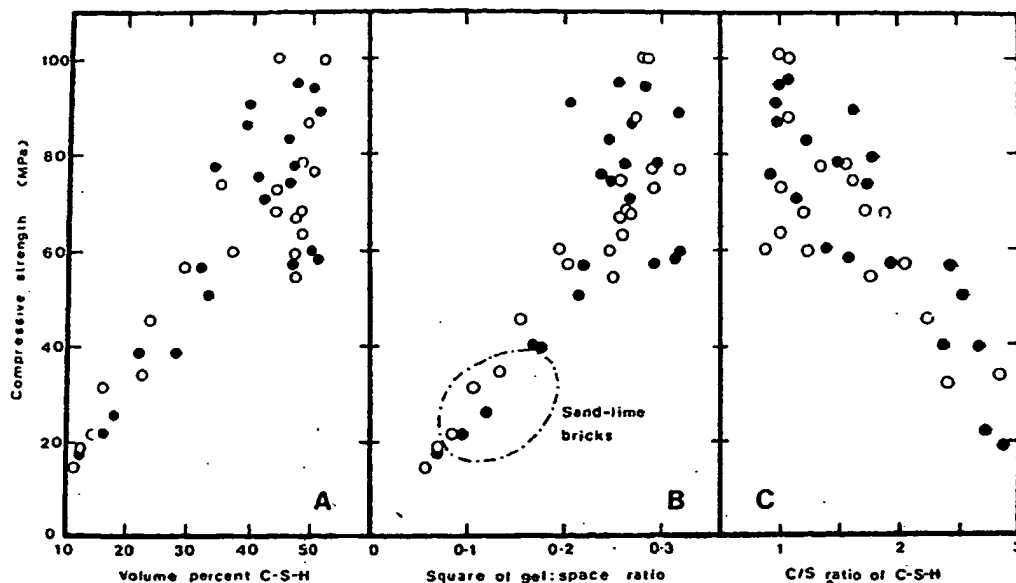


FIG. 2

Plots of compressive strength against several variables.

O Samples made without kaolinite. ● Samples made with kaolinite. Region of results for sand-lime bricks in (b) is from Purton (5).

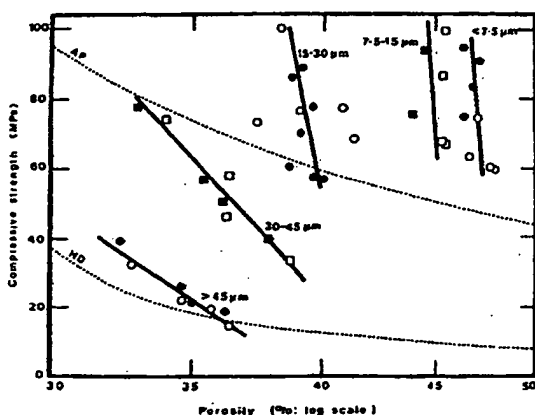


FIG. 3

Plots of compressive strength against log porosity for each quartz particle size.

O, □ Without kaolinite.
●, ■ With kaolinite.

Lines HD, AP: see text.

All these samples contain much unreacted quartz and most also contain unreacted $\text{Ca}(\text{OH})_2$. The factors that most directly control the strength are probably the porosity and the particle-size distribution of the unreacted quartz. The second of these will be fairly closely related to the particle-size distribution of the quartz before reaction, which in broad terms accounts for the high correlations in Fig. 3. The two factors together are also related to the volume of C-S-H produced, in such a way as to produce a relationship between strength and gel: space ratio that is approximately independent of the particle-size distribution of the quartz (Fig. 2b).

The reason for this independence is not clear and would repay investigation. The correlation between strength and volume percentage of C-S-H (Fig. 2a) probably arises from the higher correlation with the square of the gel: space ratio, which occurs because the variations in porosity are small relative to those in the volume percentage of C-S-H. The correlation of strength with the C/S ratio of the C-S-H (Fig. 2c) probably occurs because this ratio happens to be related to the volume percentage of C-S-H, and not because it is important in itself. The increases in strength resulting from addition of kaolinite (Fig. 1) are statistically barely significant, but appear to be due to increased production of C-S-H.

Sand-lime bricks and similar commercial materials differ from most of the samples discussed in this section in that they contain little or no unreacted Ca(OH)_2 , but resemble them in containing much unreacted quartz, with poorly-crystalline C-S-H as the binder. The same factors appear to control their strengths. Purton (5) plotted the strengths of 55 commercial sand-lime bricks against the squares of their gel: space ratios. Most of his results fall in the region shown in Fig. 2b, and are thus similar to those found in the present work.

Samples Made with Fine Quartz

For the three finest grades of quartz (15-30, 7.5 - 15 and below 7.5 μm) there are marked differences between the samples made with and without kaolinite in the trends of strength with quartz particle size and bulk C/S ratio (Fig. 1). In both groups, the highest strengths occur at or near bulk C/S 0.81 and quartz particle size 7.5 - 15 μm . However, at all bulk C/S ratios, addition of kaolinite increases the strength if the quartz particle size is below 7.5 μm , but decreases it if it is 15 - 30 μm . For all three of these grades of quartz, the porosities are influenced by the quartz particle size, but the strengths cannot be predicted with any degree of precision from the porosities (Fig. 3). It is also not possible to predict the strengths with any degree of precision from the volume percentage of C-S-H, the square of the gel: space ratio, or the C/S ratio of the C-S-H (Fig. 2). These results show that, when the finer grades of quartz are used, and the strengths are above about 55 MPa, some new factor has a major effect on the strength that is not correlated with any of the factors considered above.

In all these samples the Ca(OH)_2 has reacted completely or almost completely and more than half of the quartz has usually reacted; the weight percentages of C-S-H are mostly 70 - 90%. It is therefore not surprising that the initial particle size of the quartz no longer has a clear-cut relation to the strength. We may rather look to the characteristics of the C-S-H for an understanding of what controls the strength.

Porosity, Particle-Type Distribution and Strength

Feldman and Beaudoin (6) have proposed that the strengths of cement pastes and similar materials depend on two factors: the porosity, and the relative proportions of dense, crystalline material and less dense, poorly crystalline material. They concluded that, for any given porosity, there is an optimum

blend of these two kinds of material that gives the highest strength, and that the proportion of dense, crystalline material that is required increases as the porosity becomes less. They determined curves of log compressive strength against porosity for three types of materials, viz (i) normally cured cement pastes, (ii) materials containing predominantly dense, crystalline phases, and (iii) autoclaved cement - PFA pastes, which they considered to contain a blend of the two. Parts of their curves for materials of types (ii) and (iii) are represented on Fig. 2 by curves HD and AP respectively. It will be seen that the present results for samples made with the coarsest quartz fall near to curve HD, while those for the samples made with the three finest grades give strengths lying on or more often above curve AP. These results agree well with Feldman and Beaudoin's views. The samples made with the coarsest quartz consist largely of coarse, dense, crystalline particles, whereas in those made with the finest fractions the distribution of particle sizes, types and densities is in general better from the standpoint of strength than that represented by the curve AP.

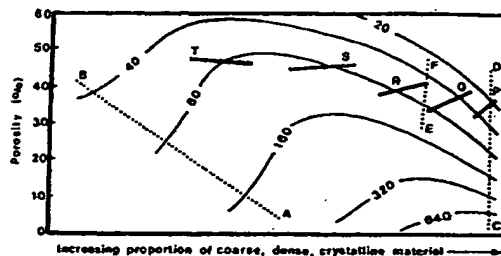
Feldman and Beaudoin's ideas can also be represented by drawing curves of constant compressive strength on plots of porosity against particle-type distribution (7), and this approach is useful in the present case. Such plots cannot be more than semi-quantitative, because the variable called particle-type distribution has not been quantified, and serves to represent several variables that are by no means perfectly correlated with each other.

Fig. 4 gives a porosity - particle type - strength plot of this type. Curves AB, CD and EF are taken from Feldman and Beaudoin's results and represent the three types of material ((i) - (iii) respectively) which they described. Lines P - T represent the present results for the five different quartz particle sizes, and are placed in positions relative to curves CD and EF that are in accord with the considerations discussed above. Several observations may be made.

(i) The diagram explains why, for the samples as a whole, the strongest tend to be the most porous; the effect of particle type outweighs that of porosity.

(ii) It explains why addition of kaolinite increases strength when the finest quartz is used but reduces it when the 15 - 30 μ m quartz is used. Several investigators have shown that addition of Al^{3+} increases the tendency of C-S-H to crystallize into tobermorite (1,8,9); further indirect

FIG. 4
Compressive strengths (MPa) as a function of porosity and particle-type distribution. Lines P - T represent results for progressively finer grades of quartz. Lines AB, CD, EF: see text.



evidence for its effect in increasing C-S-H crystallinity is provided by the observation that it reduces drying shrinkage in sand-lime bricks (10). None of the present samples contained anything that could rightly be called tobermorite, but the C-S-H crystallinity varied and tended to be higher in those made with kaolinite. The samples made with the finest quartz contain too little coarse, dense crystalline material to give the highest possible strengths for the given porosity, and addition of kaolinite therefore increases strength (Fig. 4, movement along line T). Those made with the 15 - 30 μ m quartz contain too much material of this type and addition of kaolinite therefore decreases strength (movement along line R).

(iii) The effect of over-reaction is explainable, as giving a reduction in strength due to an increase in the crystallinity or particle size of the C-S-H beyond the optimum; thus for samples made without kaolinite, lower strengths are obtained for the finest quartz (left-hand end of line T) than for the 7.5 - 15 or 15 - 30 μ m grades (left-hand ends of lines R and S).

(iv) The low correlation of strength with the square of the gel: space ratio or other variables shown in Fig. 2 can be explained by supposing that their effects are obscured by that of particle-type distribution in the C-S-H.

In conclusion, the present results fully support Feldman and Beaudoin's (6) implied conclusion that there are no "good" or "bad" binders from the standpoint of strength; a phase that gives high strengths in some situations will give low ones in others, and vice versa. There are similarly no unique answers to the questions as to whether partial crystallization of the C-S-H, or addition of Al^{3+} , improves strength.

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